Energy Barriers to Carousel Rearrangements of Carbocations: Quantum-Chemical Calculations vs. Experiment

A. M. Genaev, G. E. Sal'nikov, and V. G. Shubin

*Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,
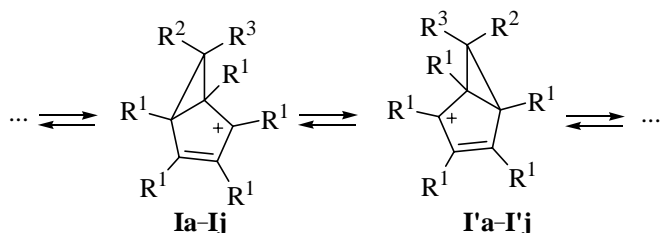Novosibirsk, 630090 Russia
e-mail: genaev@nioch.nsc.ru*

Abstract—By DFT method energy barriers were calculated for carousel rearrangements of bicyclo[3.1.0]hexenyl, cyclobutenyl, and homotropylium cations. A plausible agreement between calculated and experimental findings was found.

We formerly established [1] that quantum-chemical calculations by DFT method of energy barriers to the degenerate rearrangements of long-living carbocations occurring through 1,2-shifts of hydrocarbon migrants provided results in sufficiently good agreement with the experimental findings. In continuation of testing the adequacy of the quantum-chemical calculations for prediction of the direction and rate of carbocation rearrangements we investigated the carousel type rearrangements [2, 3]. To this end we carried out calculations of the energy barriers for the degenerate rearrangements of carbocations of the type bicyclo[3.1.0] **Ia–Ij**, **IIa–IId**, homotropylium ion **III**, and cyclobutenyl ions **IVa–IVe** (Tables 1, 2, Figs. 1–3).

The calculations show that rearrangements of cations **Ia–Ij** are one-stage processes with inversion of the migrant center configuration (as a result the *exo* and *endo* substituents of the cyclopropane fragment do not change positions). The existing experimental data for cations **Ia,**

Table 1. Energy barriers to carousel rearrangements of ions **I–III**

Cation	Barrier(calcd.), kJ mol^{-1}	$\Delta G^{\neq}$ or E_a, kJ mol^{-1}
Ia	62.6[a]	62.8 (–90°C) [4]
Ib	17.8	
Ic	76.3	> 54.4 [5]
Id	47.7	52.7 [6]
Ie	72.0	73.2 (–38°C) [7]
If	37.1[b]	43.9 [8]
Ig	35.3	41.8 [8]
Ih	33.1	41.8 [8]
Ii	43.2	56.2 (0°C) [8]
Ij	45.9	56.2 (0°C) [8]
IIa	39.1[c]	44.4 [11]
IIb	35.7	
IIc	58.0	
IId	56.6[d]	≥ 44.8 (–80°C) [12]
III	154.8	> 113[e] [13]

[a] 84 kJ mol^{-1} (4-31G) [9].
[b] 29 kJ mol^{-1} [B3LYP/cc-pVTZ//B3LYP/6-311G(d,p)] [10].
[c] ~54 kJ mol^{-1} (MNDO) [12].
[d] ~109 kJ mol^{-1} (MNDO) [12].
[e] Temperature not indicated.

Scheme 1.

$R^1 = R^2 = R^3 = H$ (**a**), Me (**f**); $R^1 = H$, $R^2 = R^3 = $ Me (**b**); $R^1 = $ Me, $R^2 = R^3 = $ H (**c**); $R^1 = R^2 = $ Me, $R^3 = $ H (**d**), Et (**g**), CH$_2$Cl (**i**); $R^1 = R^3 = $ Me, $R^2 = $ H (**e**), Et (**h**), CH$_2$Cl (**j**).

Ic–Ij [4–8] also revealed the inversion of the configuration. The calculated energy barriers of these processes (Table 1) are underestimated as compared with the experimental values on the average by 6 kJ mol^{-1}, and therewith the scatter of deviations is considerably large (from 0 to 13 kJ mol^{-1}). Nonetheless the calculations present correctly the significant difference between the barriers of the degenerate rearrangements of epimer ions **Id** and **Ie** and the insignificant difference for epimer pairs **Ig** and **Ih**, **Ii** and **Ij** (Scheme 1).

The degenerate rearrangements of cations of type **II** are also one-stage and occur without rotation of the migrant fragment. The calculated energy barriers of rearrangements of ions **IIa** and **IId** are consitent with the existing experimental findings (Table 1).

The comparison of barriers to rearrangements of carbocations of types **I** and **II** shows that the first type cations are far more sensitive to the introduction of methyl groups into the cyclopropane moiety than cations of type **II** to the introduction of these groups into their olefin fragment, and the sensitivity to the methyl group introduction into the cyclopentenyl fragment of ions of type **I** is similar to that of ions of type **II** (Scheme 2).

No precise kinetic data are available for the carousel rearrangement of homotopylium cation (**III**). It was shown in [13] by labeled atoms method that the rearrangement unlike the degenerate rearrangement of bicyclo[3.1.0]hexenyl ions proceeded very slowly ($\Delta G^{\neq} > 113$ kJ mol^{-1}). It was presumed [14] that the high barrier to the rearrangement of homotopylium cation was due to its two-stage character where the limiting stage was the cyclization stage of homotopylium ion into a bicyclo-[5.1.0]octadienyl cation (Scheme 3), cf. [15].

However our quantum-chemical calculations demonstrated that the rearrangement was one-stage. It proceeded with the inversion of the comfiguration at the atom C^8, and its energy barrier amounted to 155 kJ mol^{-1} (cf. [9, 16, 17]). The conclusion on the inversion of the configuration at the atom C^8 in the course of this rearrangement was published before [17, 18].

Our calculations showed that the degenerate rearrangements of type **IV** ions, except ion **IVa**, were two-stage. They proceed with the formation of cyclopropenyl-carbinyl intermediates of type **V** (for **IVa** it was not an intermediate but a transition state on a gently sloping plateau) (Scheme 4).* This mechanism was formerly

*The relation of ions **IVa–IVe** to ions I and **II** is revealed in Scheme 4 by showing them as resonance structures with a cyclopropane fragment.

Scheme 2.
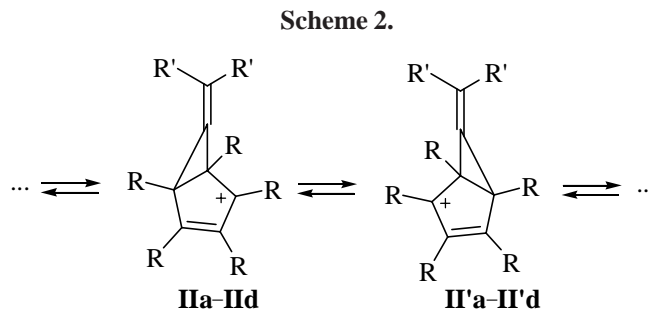
R = R' = H (**a**), Me (**d**); R = H, R' = Me (**b**); R = Me, R' = H (**c**).

Scheme 3.
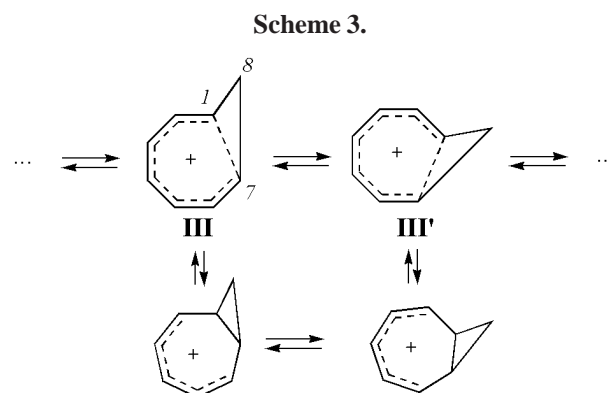
assumed in [19, 20], and the formation of type **V** structures in the course of the degenerate rearrangement of type **IV** ions was calculated ab initio [18, 21].

The calculations by DFT method predict that the energy barrier to the degenerate rearrangement of cation
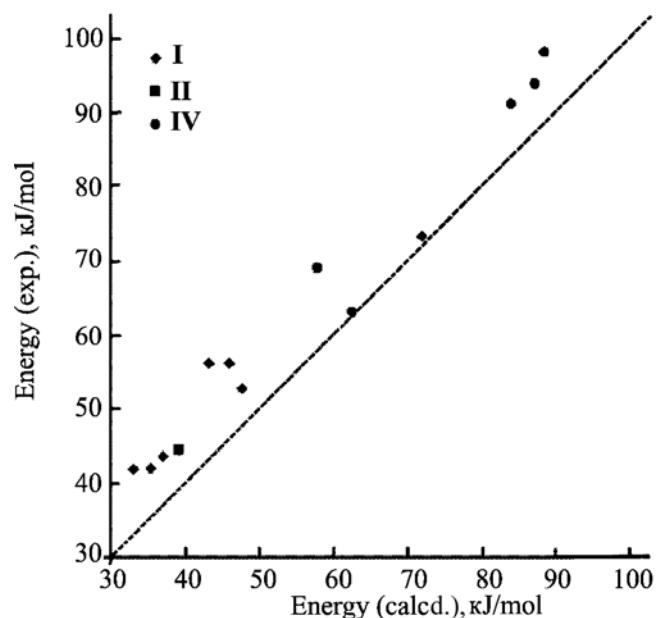

Fig. 1. Comparison of experimental and calculated data. The dotted line is drawn at the angle 45°.

Table 2. Relative energies of ions **IV** and **V** and of transition states (TS) in their rearrangements

Structure	Relative energy (calcd.), kJ mol^{-1}	$\Delta G^{\neq}$(exp.), kJ mol^{-1}
IVa	0.0	
Va (TS)	106.9[a]	
IVb	0.0	
TS **IVb ⇆ Vb**	57.8	68.9 (27°C)[b]
Vb	34.3	
TS **IVb ⇆ Vc**	84.2	91.2 (20°C)
Vc	70.9	
TS **Vc ⇆ IVc**	77.6	
IVc	−12.8	
IVd	0.0	
TS **IVd ⇆ Vd**	87.3	94 (30°C)[b,c]
Vd	77.5	
IVe	0.0	
TS **IVe ⇆ Ve**	88.5	98 (20°C)[b,c]
Ve	77.4	
IVf	0.0	
TS **IVf ⇆ Vf**	62.6	≈63 [24]
Vf	46.1	

[a] 112 kJ mol^{-1} (4-31G) [18], cf. [20, 23].

[b] In calculation of $\Delta G^{\neq}$ the statistical factor equal two was taken into account.

[c] Calculated by Eyring equation from the rate constants of degenerate rearrangements estimated from the data of [19]: for ion **IVd** k 2× 10^{-4} s^{-1} (30°C), for ion **IVe** k × 10^{-5} s^{-1} (20°C).

Scheme 4.
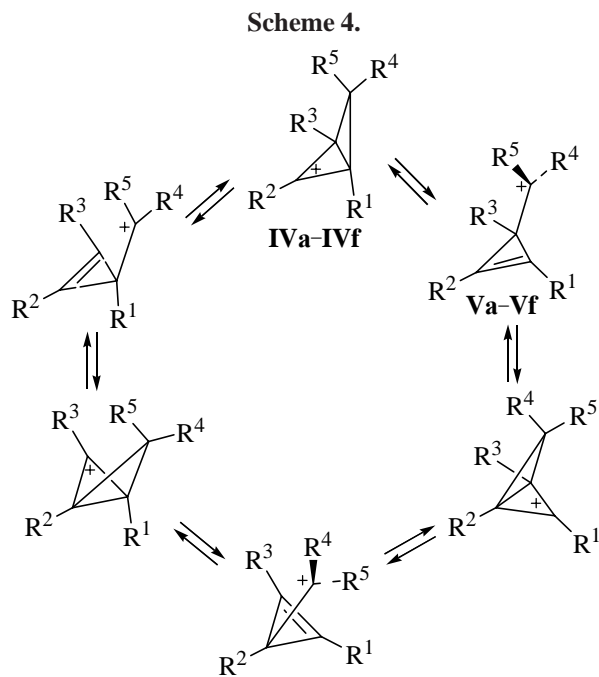
R^1 = R^2 = R^3 = R^4 = H, R^5 = Me (**a**); R^1 = R^2 = R^4 = R^5 = Me, R^3 = H (**b**); R^1 = R^3 = R^4 = R^5 = Me, R^2 = H (**c**); R^1 = R^2 = R^3 = R^4 = R^5 = Me (**d**); R^1 = R^2 = R^3 = R^5 = Me, R^4 = i-Pr (**e**); R^1 = R^2 = R^3 = R^5 = t-Bu, R^4 = OH (**f**).
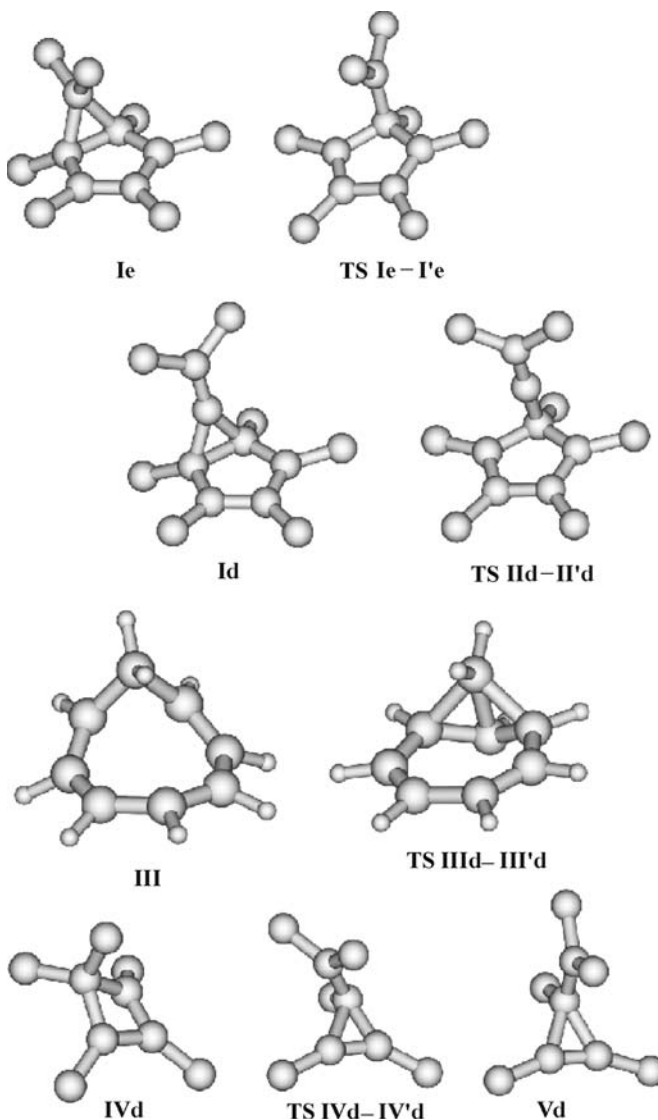
Fig. 2. Calculated structures of cations and transition states in carousel rearrangements of ions **I–IV**. Hydrogen atoms of the methyl groups are not shown.

IVb is relatively low (Table 2, Fig. 1). Therefore it was presumable that the lacking experimental value of the energy barrier to this rearrangement might be measured by dynamic NMR. Actually, at heating the solution we observed in the ^{1}H NMR spectrum of ion **IVb** a reversible broadening of the signals of 1- and 2-methyl groups corresponding to the degenerate rearrangement of the ion (at 27°C Δ 1.0 Hz, k 3.1 s^{-1}).*

Like in the case of type **I** cations, the calculations somewhat underestimate the energy barriers of the degenerate rearrangement compared with the experi-

*Cation **IVb** is unstable at higher temperature [19, 22].

Table 3. Chemical shifts (δ, ppm) and energy of ion **IVe** conformers

	1,3-Me	2-Me	4-Me	Me (*i*-Pr)	H (*i*-Pr)	Relative energy, kJ mol^{-1}
IVe-1	2.54	2.42	1.29	1.29	1.81	0.0
IVe-2	2.51	2.43	1.46	0.95	2.77	0.4
IVe-3	2.58	2.38	1.76	1.24	1.94	9.5
Experiment	2.6	2.4	1.4	1.1	2.3	

mental values (Table 2, Fig. 1). The calculations give a correct prediction of the sequence of transformations observed at the ionization of carbinol **VI** [19, 22] (Scheme 5, Fig. 3).

For ion **IVe** the calculations reveal three conformations (Scheme 6), and two of them (**IVe**-1, **IVe**-2) with an *exo*-position of the isopropyl group are more stable (Table 3) and possess very close energy. Inasmuch as the interconversion of these conformations by rotation of the isopropyl group aroung the C–*i*-Pr bond is evidently a fast process it is expectable that the chemical shifts observed in the ¹H NMR spectrum should be intermediate between the chemical shifts corresponding to these conformations. Actually, the calculated data are well consistent with the experimental findings (Table 3).

The comparison of data on the energy barriers to the degenerate carousel rearrangements calculated by DFT method with the experimental findings (Fig. 1) shows that in most cases the calculations underestimate the barrier values. Nonetheless, the calculated data are fit to make estimation of the barriers.

Scheme 5.

Scheme 6.

IVд-1   IVд-2   IVд-3
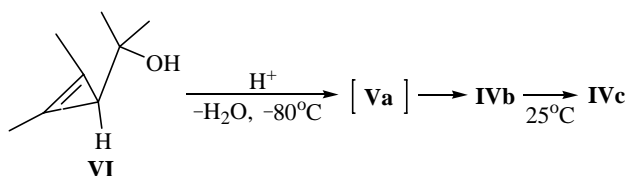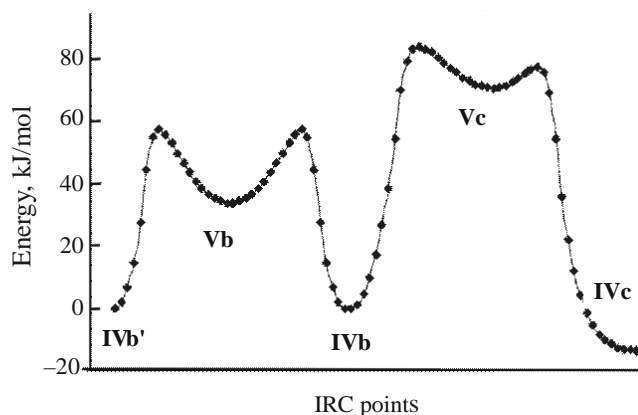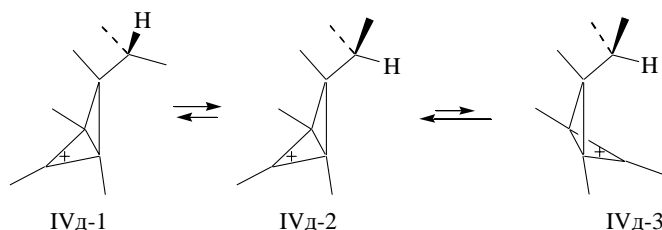
Fig. 3. The section of potential energy surface for the rearrangement of ions **IVb** and **IVc** calculated with the use of IRC (Intrinsic Reaction Coordinate).

EXPERIMENTAL

Quantum-chemical calculations of the geometry and energy of carbocations were performed by DFT method (functional PBE [25]) using program "Nature" [26] {basis 3z, (11s6p2d)/[6s3p2d] for C and (5s1p)/[3s1p] for H}. The calculation procedure is described in [1].

The rate constant of nondegenerate rearrangement **IVb→IVc** was measured by ¹³C NMR from the variation of the intensity ratio of methyl signals of these ions [22]: $k\ 3.4 \times 10^{-4}\ \text{s}^{-1}$ (20°C). The rate constant of the degenerate rearrangement of ion **IVb** was calculated by the formula $k = \pi\Delta$, where Δ is the exchange broadening of signals of the ion generated at –70°C by procedure [19, 22].

REFERENCES

1. Genaev, A.M. and Shubin, V.G., *Izv. Akad. Nauk, Ser. Khim.*, 2006, p. 1045.
2. Childs, R.F., *Tetrahedron,* 1982, vol. 38, p. 567.
3. Klärner, F-G., *Top. Stereochem.*, 1984, vol. 15, p. 1.
4. Vogel, P., Saunders, M., Hasty, N.M. Jr., and Berson, J.A., *J. Am. Chem. Soc.,* 1971, vol. 93, p. 1551.
5. Childs, R.F. and Winstein, S., *J. Am. Chem. Soc.,* 1968, vol. 90, p. 7146.
6. Koptyug, V.A., Kuzubova, L.I., Isaev, I.S., and Mamatyuk, V.I., *Zh. Org. Khim.*, 1970, vol. 6, p. 2258.
7. Childs, R.F. and Winstein, S. *J. Am. Chem. Soc.*, 1974, vol. 96, p. 6409.

8. Isaev, I.S., Mamatyuk, V.I., Kuzubova, L.I., and Gordymova, T.A., *Zh. Org. Khim.*, 1970, vol. 6, p. 2482.

9. Hehre, W., *J. Am. Chem. Soc.*, 1974, vol. 96, p. 5207.

10. Arstad, B., Kolboe, S., and Swang, O., *J. Phys. Chem. A*, 2005, vol. 109, p. 8914.

11. Jarret, R.M., Saunders, M., Pikulin, S., and Berson, J.A., *J. Am. Chem. Soc.*, 1986, vol. 108, p. 2768.

12. Shubin, V.G., Shakirov, M.M., Nagy, S.M., and Osadchii, S.A., *Mendeleev Commun.*, 1992, p. 110.

13. Berson, J.A. and Jenkins, J.A., *J. Am. Chem. Soc.*, 1972, vol. 94, p. 8907.

14. Scott, L.T. and Brunsvold, W.R., *J. Am. Chem. Soc.*, 1978, vol. 100, p. 6535.

15. Childs, R.F., *Acc. Chem. Res.*, 1984, vol. 17, p. 347.

16. Hehre, W., *J. Am. Chem. Soc.*, 1972, vol. 94, p. 8908.

17. Barzaghi, M. and Gatti, C., *J. Mol. Struct. THEOCHEM.,* 1988, vol. 166, p. 431.

18. Hehre, W.J. and Devaquet, A.J.P., *J. Am. Chem. Soc.*, 1976, vol. 98, p. 4370.

19. Shleider, I.A., Isaev, I.S., and Koptyug, V.A., *Zh. Org. Khim.*, 1972, vol. 8, p. 1337.

20. Kelsey, D.R., *J. Chem. Res. Synop.,* 1986, p. 44.

21. Minkin, V.I., Dorogan, I.V., and Minyaev, R.M., *Zh. Org. Khim.,* 1998, vol. 34, p. 1602; Minkin, V.I., Dorogan, I.V., and Minyaev, R.M., *J. Phys. Org. Chem.*, 2000, vol. 13, p. 3.

22. Salnikov, G.E., Genaev, A.M., and Mamatyuk, V.I., *Mendeleev Commun.*, 2003, p. 48.

23. Morio, K. and Masamune, S., *Chem. Lett.,* 1974, p. 1251.

24. Maier, G., Emrich, R., and Kalinowski, H.-O., *Angew Chem. Int. Ed.,* 1985, vol. 24, p. 429.

25. Perdew, J. P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 1996, vol. 77, p. 3865.

26. Laikov, D.N., *Chem. Phys. Lett.*, 1997, vol. 281, p. 151; Laikov, D.N. and Ustynyuk, Yu.A., *Izv. Akad. Nauk, Ser. Khim.,* 2005, p. 804.